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**APPLICATION NUMBER: 60/541,101**

**FILING DATE: *February 02, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/03389***



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17236 U.S. PTO

Customer No. 31013

Docket No. 161485-00680

**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

Mail Stop Provisional Patent Application  
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P.O. Box 1450  
Alexandria, VA 22313-1450

This is a request for filing a Provisional Application for Patent under 37 C.F.R. § 1.53(c).

Inventor(s) and Residence (city and either state or foreign country):

Timothy Thomson - West Newbury, Massachusetts

For **USE OF POLAR POLYURETHANE AS A SOLID SOLVENT EXTRACTANT**

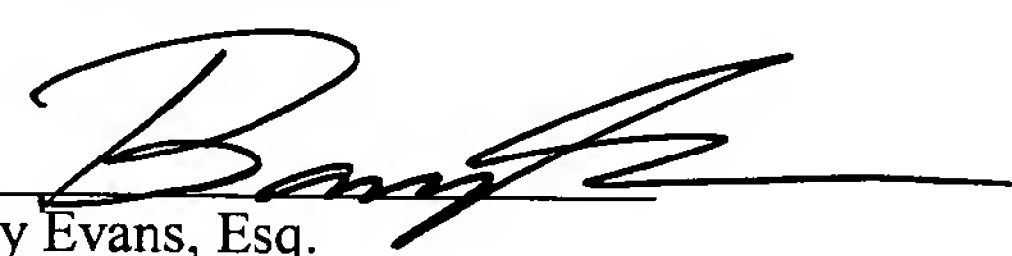
1. ☒ 10 sheets of specification
2. ☒ A check in the amount of \$80.00 is enclosed in payment of the required fee. The Commissioner is hereby authorized to charge and additional fees or credit any overpayment to Deposit Account No. 50-0540.
3. ☒ Please direct all communications relating to this application to the address of:

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4. ☒ Applicant hereby states pursuant to 37 C.F.R. § 1.27(c)(1) that Applicant is a small entity.
5. ☒ This invention was not made by an agency of the United States Government or under a contract with an agency of the United States Government.

Dated: February 2, 2004

Respectfully submitted,

By:   
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31355 U.S. PTO  
60/541101



Customer No.: 31013

Docket No.: 161485-00680

**PROVISIONAL APPLICATION FOR LETTERS PATENT**

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Title: **USE OF POLAR POLYURETHANE AS A SOLID SOLVENT  
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### **Background of the Invention**

A natural and seemingly inevitable result of industrial development and human activity is the release of organic and inorganic contaminants to the environment. Industrial development has led to the release of contaminants that range in toxicity from benign to acute to chronic. Agricultural progress, especially in the control of insects and weeds, led to well-known pollutants.

Most of these contaminants are destroyed naturally by the biosphere. Naturally occurring clays and rocks are able to remove many pollutants from the water by ion exchange and adsorption processes. Bacteria, molds, and algae all have the ability to metabolize pollutants. Septic tanks and municipal water waste treatment facilities depend on the bacteria to degrade human waste. When new pollutants are introduced into the environment, microorganisms, in most cases, evolve to use the contaminant as a food source.

The concentration of population in urban areas and large releases of industrial waste in many cases, however, have out-stripped the ability of the environment to handle the level of pollutants released. There are also classes of synthetic organic pollutants that have been designated recalcitrant in the sense that the natural environment does not seem capable of removing them. Halogenated hydrocarbons and certain pesticides are in this category.

These contaminants are found in water resources and in the air in populated areas fares no better. The concentration of polycyclic aromatic hydrocarbons (PAH) was measured in the air around Chicago and Houston.

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PAH	Chicago	Houston
Acenaphthalene	76.9	22.8
Fluorene	74.8	24.2
Phenanthrene	200	50.1
Anthracene	14.1	1.4
Fluoranthene	44.1	10.2

The US Department of Agriculture monitors the pesticide concentrations in ground water that result from agricultural run-off. The chlorine and phosphate-based chemicals are among the most toxic releases. An added complication is that these are non-point source releases i.e. there is not an identifiable release point that can be controlled.

Many of these organic, and in some cases inorganic, chemicals have a potential for bioaccumulation or, much worse, present acute toxicity to the populace. Despite this, there is still a lack of effective means for remediation.

Among the processes used to treat water to remove contaminants are steam distillation, extraction, adsorption on activated charcoal, chemical oxidation various biological and membrane techniques. In the latter category are treatment with microorganisms, reverse osmosis and treatment with enzymes.

Air can be injected into the soil around the aquifer and recovered in sorption towers for concentration and removal from the environment. Alternatively water can be pumped from the contaminated aquifer through sorption columns and re-injected into the ground water system (local regulations not withstanding). In this context sorption means any process by which the fluid (air or water) is contacted with a material for which the pollutant has an affinity. The

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affinity can be a physical trapping modified by some form of surface energy or a solvent extraction process. The result is that the fluid is pumped through the sorption medium and the pollutant is reduced or eliminated from the fluid.

The most common sorption medium is activated charcoal. Activated charcoal is charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atoms. These so-called active, or activated, charcoals are widely used to adsorb odorous or colored substances from gases or liquids.

When certain chemicals pass next to the carbon surface, they attach to the surface and are trapped. Activated charcoal is good at trapping other carbon-based impurities (organic chemicals), as well as inorganics like chlorine. Many other chemicals are not attracted to carbon at all -- sodium, nitrates, etc. -- so they pass through a bed of charcoal unaffected. Once all of the bonding sites are filled, however, an activated charcoal filter stops working.

Other extraction systems involve contacting the contaminated fluid (air or water) with a solvent for the pollutant. A solvent must be used that is environmentally acceptable (e.g. biodegradable) or special precautions must be taken to ensure that the solvent is not released to the environment.

Biphasic extraction media, i.e. homopolymers and copolymers made from ethylene oxide and blends of ethylene oxide and propylene oxide, respectively, can be used as purification media. Because they are soluble in water, in themselves, they are not useful in a solvent extraction scheme. In order for them to be effective, once the extraction process is produced it is necessary to separate a phase containing the pollutant, thus removing it from water. While these compounds can be used to extract contaminants from air, their water solubility precludes their use in purifying ground water. In the biphasic system, separation is

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achieved by the well-known physical chemical effect known as "salting out". Inorganic salts are added to the system. This has the effect of "dehydrating" the polyol, thus making it insoluble and permitting separation.

Part of their suitability is that they are of variable molecular weight. At low molecular weight they are both water-soluble, but as the molecular weight increases, the polypropylene glycol is water insoluble. The extra methyl group prevents significant hydration. One of the most attractive features of this chemistry is that it is relatively benign, environmentally speaking. Separation of the phases are possible, but problematic, on a large scale.

Hydrophobic polyurethanes for use in water purification processes has been described by El Shahawi et al El-Shahawi,-M.S., et al, Preconcentration and separation of some organic water pollutants with polyurethane foam and activated carbon. 19. Int. Symp. on Chromatography, Aix-en-Provence (France) 13-18 Sep 1992 CHROMATOGRAPHIA 1993 vol. 36, pp. 318-322. The author studied the use of polyurethane for the extraction of pesticides and similar compounds from water. He reported on an investigation of the extraction of Dursban, Karphos and Dyfonate by activated charcoal and a polyether polyurethane foam. El Shahawi, et al observed that as the polarity of the pesticide increases, the ability of polyurethane to extract it decreases. El Shahawi used hydrophobic (nonpolar) polyether polyurethanes for his work.

### **Summary of the Invention**

It has now been discovered that a hydrophilic or polar polyurethane can extract sparingly soluble organic chemicals from water and air. Still further, the grafting of the

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polyurethane onto a reticulated scaffold provides for a high surface area device with excellent flow-through properties.

We have found that reacting the terminal hydroxyl groups of the polyglycols with polyisocyanates and then reacting the isocyanate-capped polyglycols with water produces a so-called hydrophilic polyurethane with the extraction abilities of the iphasic polyglycol, but in an insoluble form. This, thereby, avoids the problematic "salting out" process and makes the system less temperature sensitive.

Preferably, the polyglycol is a homopolymer of ethylene glycol or a copolymer of polyethylene oxide and polypropylene oxide, the polypropylene oxide being no more than 90% of the total mass. The hydroxyl functionality of the polyols is preferably two or more. The isocyanate be preferably toluene diisocyanate, methylene bis diphenyl diisocyanate, isophorone diisocyanate or other commercially available polyisocyanate

This polymer system is particularly effective at extracting sparingly soluble organic molecules from air and water. By adjusting the relative amounts of propylene oxide and ethylene oxide, one can effectively affect the dipole moment of the system and therefore control the classes of compounds that are extractable. We have also found that grafting the copolymer onto an open cell foam, is a scaffold, a flow-through, high surface area system is produced, making the extraction process more convenient.

An examination of the literature in this area revealed that, while research on the use of polyurethanes is known, it is limited to the removal of hydrophobic chemicals. The polyurethanes used for the extractions are made from conventional hydrophobic polyethers and polyester polyols.

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In Figure 1, we show the extraction of the polar dye bromothymol blue by a hydrophobic (nonpolar) polyether polyurethane. In Figure 2, we show the extraction by a polar polyurethane made from the reaction of polyethylene glycol, a polyisocyanate and water. The polyurethanes were immersed in a 0.05% bromothymol blue solution. Evidence of extraction would have been a decrease in the absorption of visible light, as is evidenced from the spectra of Figure 2.

The typical color response of bromothymol blue to changes in pH is maintained when it is extracted onto the subject polar polyurethane. When extracted onto the hydrophobic polyurethane, it is no longer pH sensitive.

In the following study, a polar polyurethane, made as described above, was grafted to a 30 pore per inch reticulated foam as taught by Thomson in U.S. Patent No. 6,617,014. The foam was loaded into columns (described below) and a 100ppm solution of methyl-tert-butylether (MtBE, a polar organic compound) was pumped through it. The experiment is further described as follows:

- Length = 280 cm
- Inside Diam. = 4.0cm
- Volume = 3.5 liters
- Foam Capacity = 420 grams (typical)
- Wt. Hydrophilic Foam = 300 grams (typical)
- Flow Rate = 0.05 liters/min (typical)
- Fixed Rate Peristaltic Pump
- Temperature = 15-45°C (typical)
- Control and Data Acquisition = Workbench on Macintosh Platform
- Analytical = Gas Chromatograph and UV-VIS Spectrophotometry
  - Concentration= 100ppm MtBE

The MtBE solution was pumped through the columns. The effluent was analyzed to detect the first MtBE eluting. This was termed break-through and was used to calculate the “capacity” of the polymer. From these data it was determined that the column could extract

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about 3.5mg MtBE per gram of the subject polymer. The columns were drained and purged with air heated to 65°C overnight. The MtBE solution was again pumped through the columns and the break-through determined. It was found that the columns recovered the capacity to adsorb ca. 3.5 mg/gram. The ability to regenerate the column is thus confirmed.

In another experiment, we showed that fragrances wafting through the air in a closed chamber could be extracted by the polar polyurethane but not the conventional non-polar polyurethane. A sample of a commercial perfume was placed in a vessel in the chamber shown in Figure 3. Samples of hydrophobic polyurethane and the subject polymer were placed in the chamber for an hour. Regardless of the distance from the vessel, the polar polyurethanes showed evidence of extraction (by odor) while the non-polar samples showed none.

In another experiment using hydrophilic polyurethane, we showed the extraction of fabric dyes from washing machine water. Six extra large men's sweaters (three dark blue, one red and one green) were washed using the recommended procedures in a household washing machine using a commercial detergent. Several pieces of hydrophilic polyurethane foam were placed in the washer along with the sweaters. After a standard cycle the hydrophilic foam was removed and the color was examined (Figure 4).

While these examples show the general characteristics of the invention, it will be obvious to those knowledgeable in the art that other polar compounds will be extracted upon contact with subject polar polyurethane.



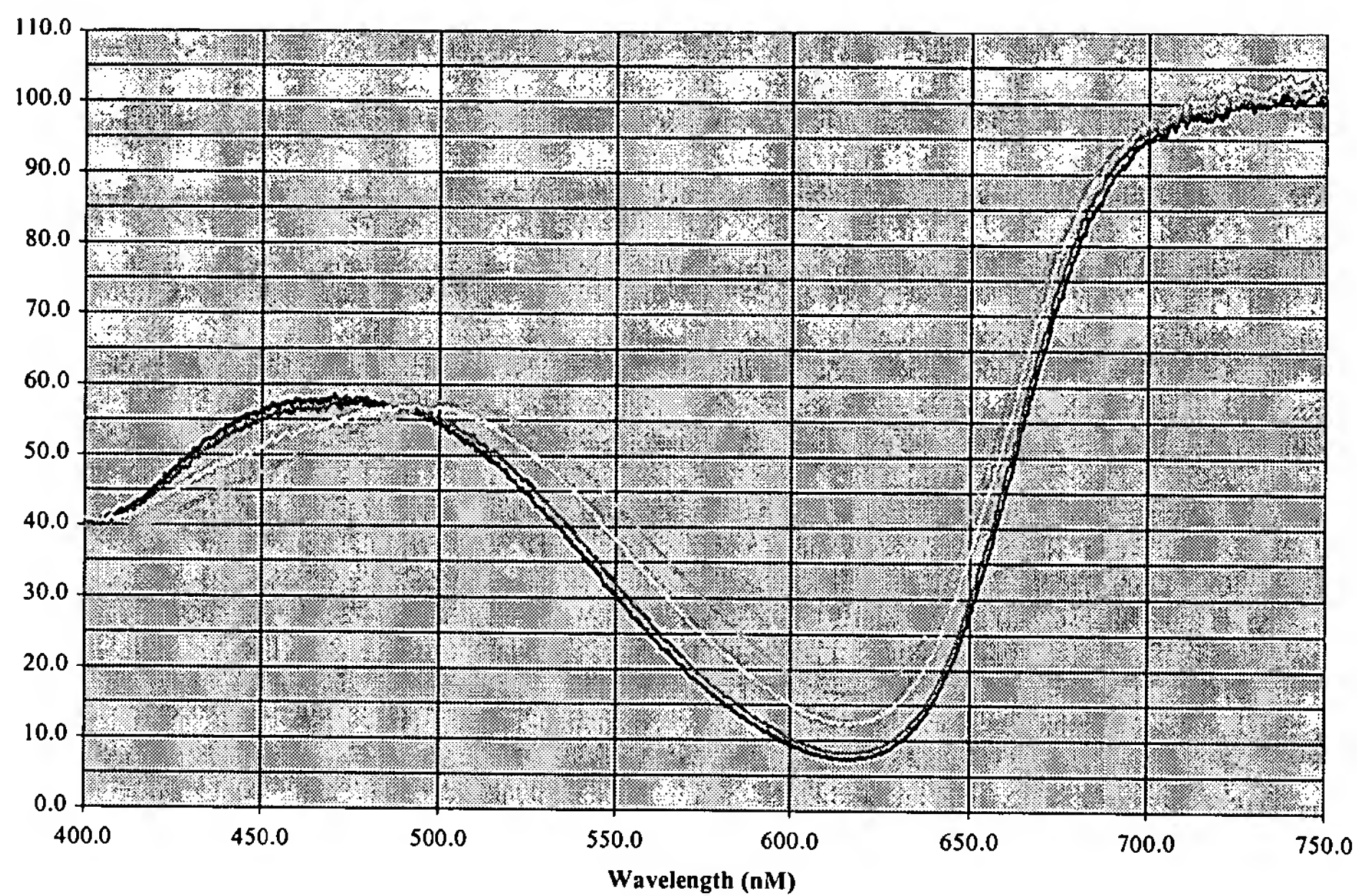


FIGURE 1: No Extraction of Bromothymol

Blue by a Non-polar Polyurethane

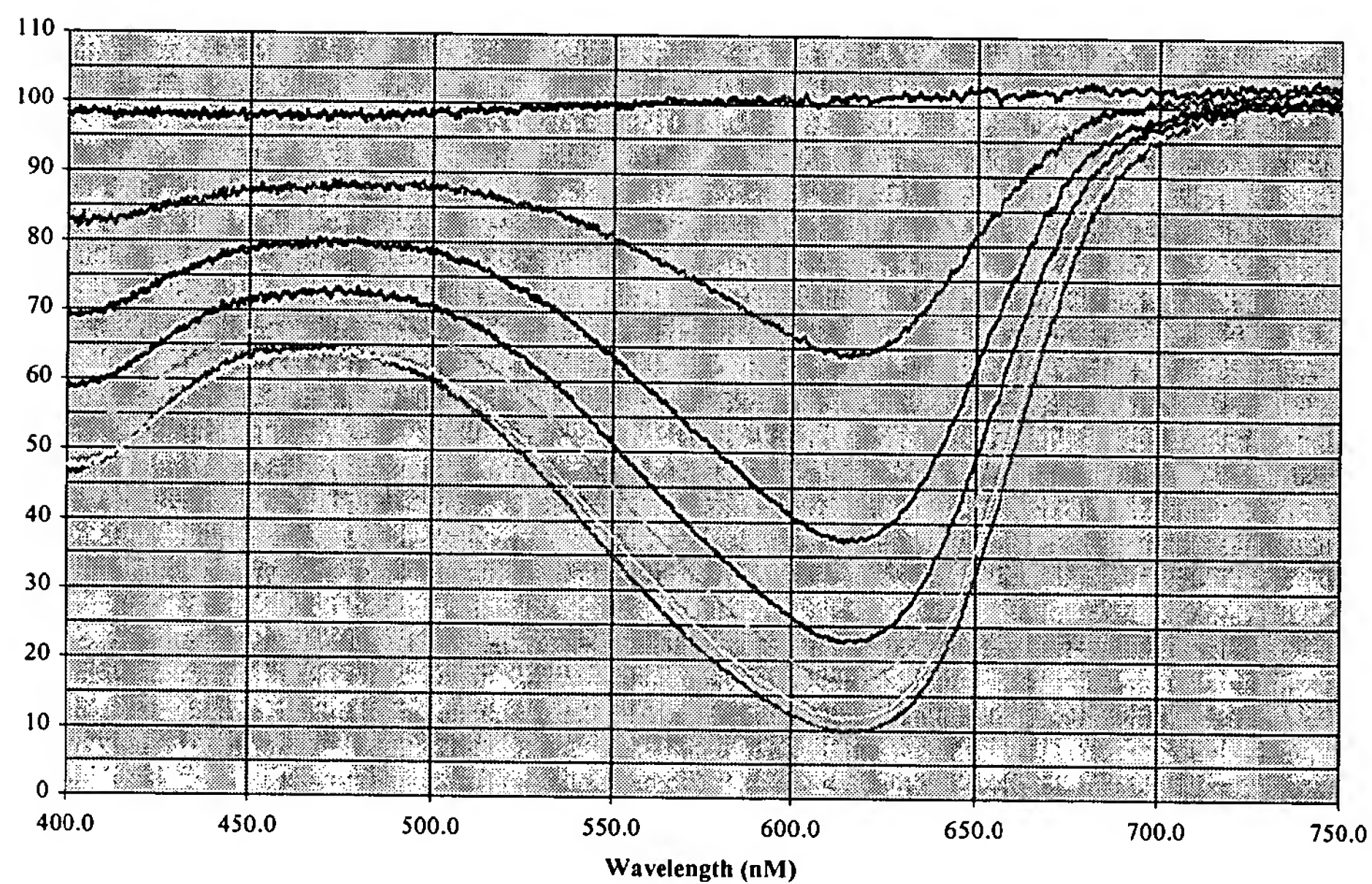


FIGURE 2: Extraction of Bromothymol

Blue by the Polar Polyurethane

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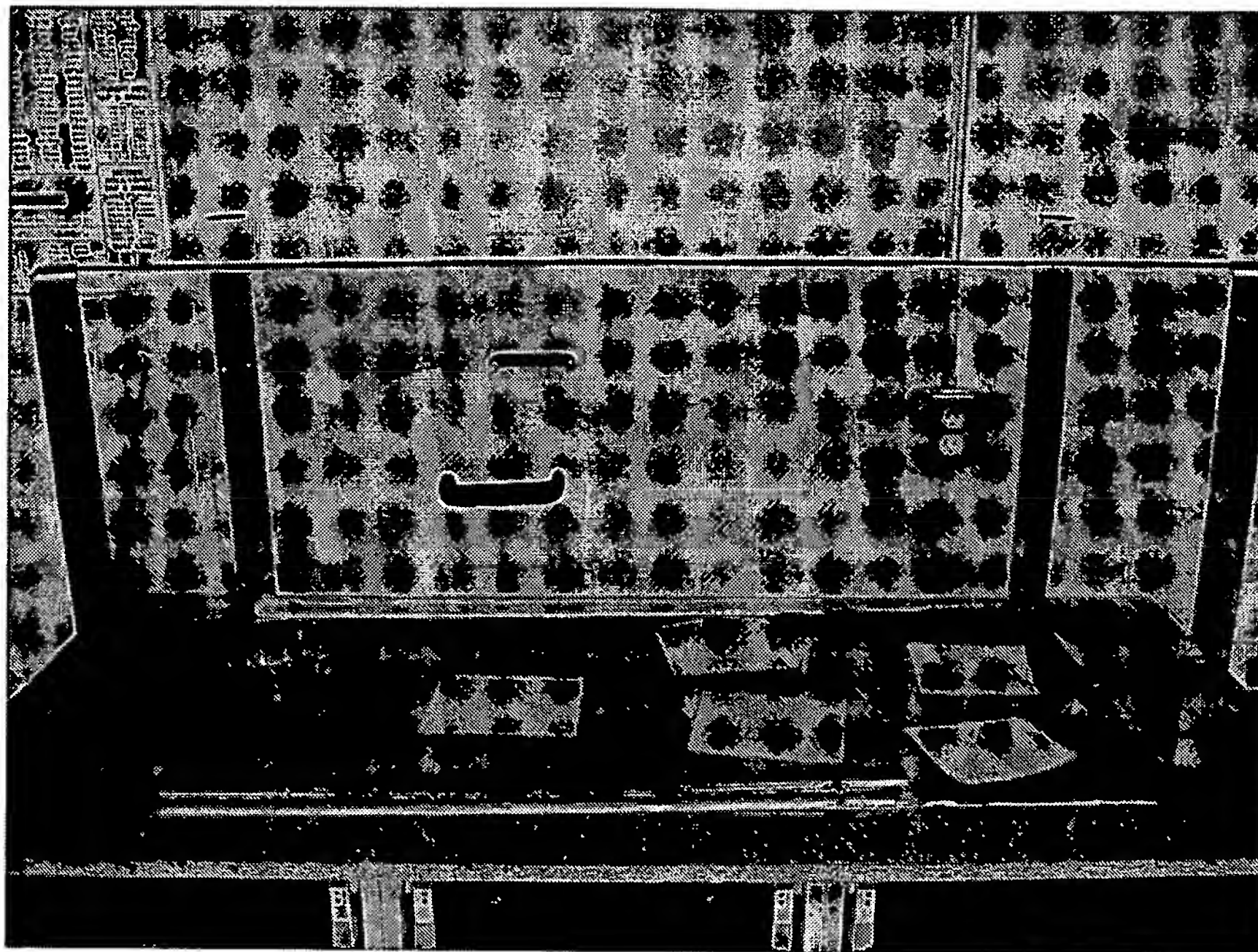


FIGURE 3: Odor Extraction  
Experiment

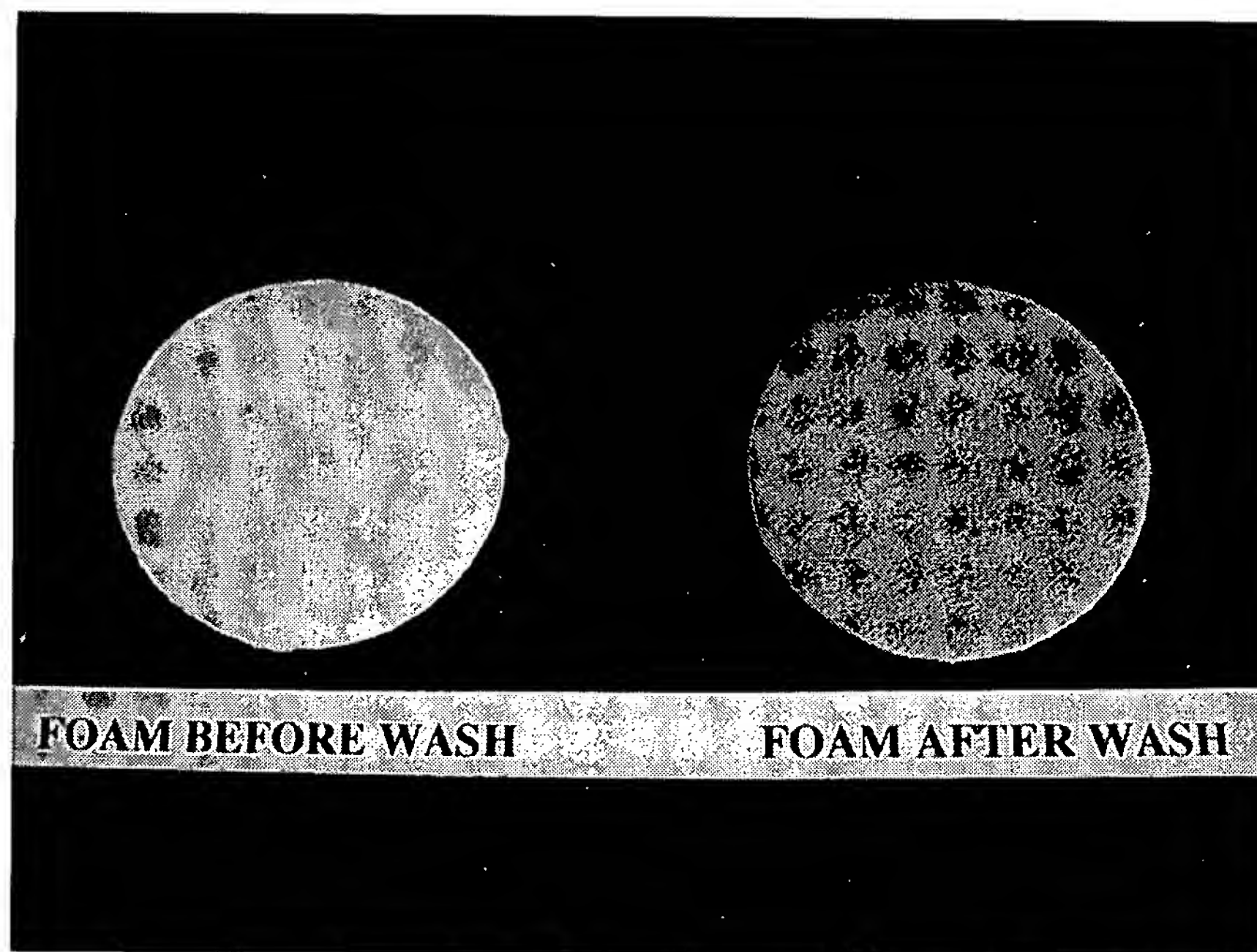


FIGURE 4: Evidence of the extraction of  
fabric dyes by hydrophilic polyurethane

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